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THE COMPATIBILITY OF VARIOUS METALS WITH MHF-3

by

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ABSTRACT. The compatibility of various pure metals with MHF-3 was determined at 74°C (165°F). Metals investigated included titanium, copper, iron, aluminum, and nickel in the annealed and cold-worked conditions, and chemically deposited chromium. Tests were conducted in an all pyrex, torch-sealed pressure vessel. Pressure changes were recorded over a 94 day period. Post exposure evaluations of the metals were made by electron microscopic examination, microprobe analysis, and tensile tests.

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FOREWORD

This report constitutes the final report summarizing the effort on the compatibility of high purity metals with MHF-3 liquid and vapor environment. This program was initiated in July 1969 and was conducted under AirTask WF 19.333.301, W.U. 40 by the Propulsion Technology Division.

This report was reviewed for technical accuracy by Dean H. Couch, Code 4584.

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INTRODUCTION

Because of the reactive nature of most liquid propellants, practically all adjacent metal components are susceptible to corrosion; or the propellant itself is degraded under long term storage. Some of the new high energy propellants are extremely reactive and their compatibility with metals has not been systematically investigated. Because of this, there is a minimum of reliable engineering data as well as fundamental information on liquid propellant-metal compatibility.

A program has been initiated to determine the compatibility of various metals with Navy storable liquid propellant fuels. Phase 1 of this program, now completed and described herein, deals with the compatibility of various pure metals with MHF3[1] at 74°C (165°F).

Testing was divided into two general sections. Section 1 involved determining propellant decomposition rates by measuring the pressure generated by reaction of the various metals with MHF-3. Section 2 involved studying the effect of storage on the various metals. Properties considered were static tensile and yield strengths, ductility, surface appearance, microstructure and deposits from metal-propellant reaction.

EQUIPMENT AND PROCEDURE

APPARATUS

A method often used in studying the chemical stability of liquid propellants with various materials is to expose the samples to different temperatures for various periods in closed containers, and observe pressure development. The methods of measuring the pressure include mercury manometers and the common metal Bourdon tube pressure gages. In both cases, the propellant is usually exposed either as vapor and/or liquid to mercury or to the metal Bourdon tube. Previous work has shown that pure mercury does not influence the stability of the propellants, but there is always a question about the changes in purity. In the case of the metal Bourdon tube the stability of the propellant is admittedly affected, but often a series of tests is made with the hope of minimizing or somehow compensating for this effect. Isolating fluids have been used to separate the measuring device from the propellant. However, the effect of these fluids on the propellant stability is uncertain and the propellant may diffuse through the isolating media.

[1] Military Specification Propellant, Mixed Hydrazine Fuel. MHF-3, MIL-P-81342(WP), 10 December 1965.

Another problem encountered with the metal Bourdon tube gages with pipe threads is propellant leakage. Pipe threads cannot always be sealed, especially to hydrogen, and the use of thread sealants introduces other unknowns. This sealing problem can be solved by using a metal bellows or wafer which is welded in place between the gage and the sample container. Likewise, the filling tube can be crimped and welded shut. This method gives a positively closed system with the added advantage of exposing the propellant to only the metal of interest, including the necessary weld areas. Another method of sealing the all-in-one metal containers used in vacuum studies is that in which a closure wafer is V-crimped into the base metal by a flange made of harder metal. This offers a less positive seal than the welded method, but is more suitable for short term studies where small samples are required and where post-test sample inspection is desired. In each of these all-metal containers, the pressure gages must be vacuum-filled with a suitable high boiling point fluid so that the gage will respond to the pressure developed in the container. The increase in volume of the Bourdon tube (2 to 3%) as the pressure rises must be considered since the bellows or wafer has to move this amount without appreciable pressure drop.

In view of all these problems and the need for a device which could be used for laboratory studies of both propellant stability and compatibility, an all-glass pressure indicating container was developed. This container is called a Staco cell (Ref. 1) and is shown in Fig. 1. The original cell consists of a 5-cm diameter glass sample container of whatever length is needed, and 5-cm diameter extension guard to protect a glass Bourdon tube pressure indicator and a filling tube that is torch sealed. Two small, front-surfaced aluminized mirrors are used with a galvanometer or laser type light source and scale (reading stand) to read pressure (Fig. 2). The reference (zero) mirror is attached to the wall of the guard tube. The pressure indicating mirror is attached to the end of the glass Bourdon tube. Each Staco cell must be calibrated in the reading stand since manufacture of the glass Bourdon tubes cannot be exactly duplicated. The data obtained in this program were obtained with the original cell design. The modified Staco cell is an improved version and will be used for subsequent tests. The mirrors on this model are fused in place, thus eliminating any possibility of mirror drift. A plastic removable guard tube is slipped over the top of the cell for protection of the Bourdon-mirror assembly.

The Staco cells offer a number of advantages:

1. They can be positively sealed.

2. The tip of the sealed tube can be broken off inside a piece of plastic tubing so the "total" samples, gases and liquid can be transferred to analysis equipment.

3. The sample can be visually observed.

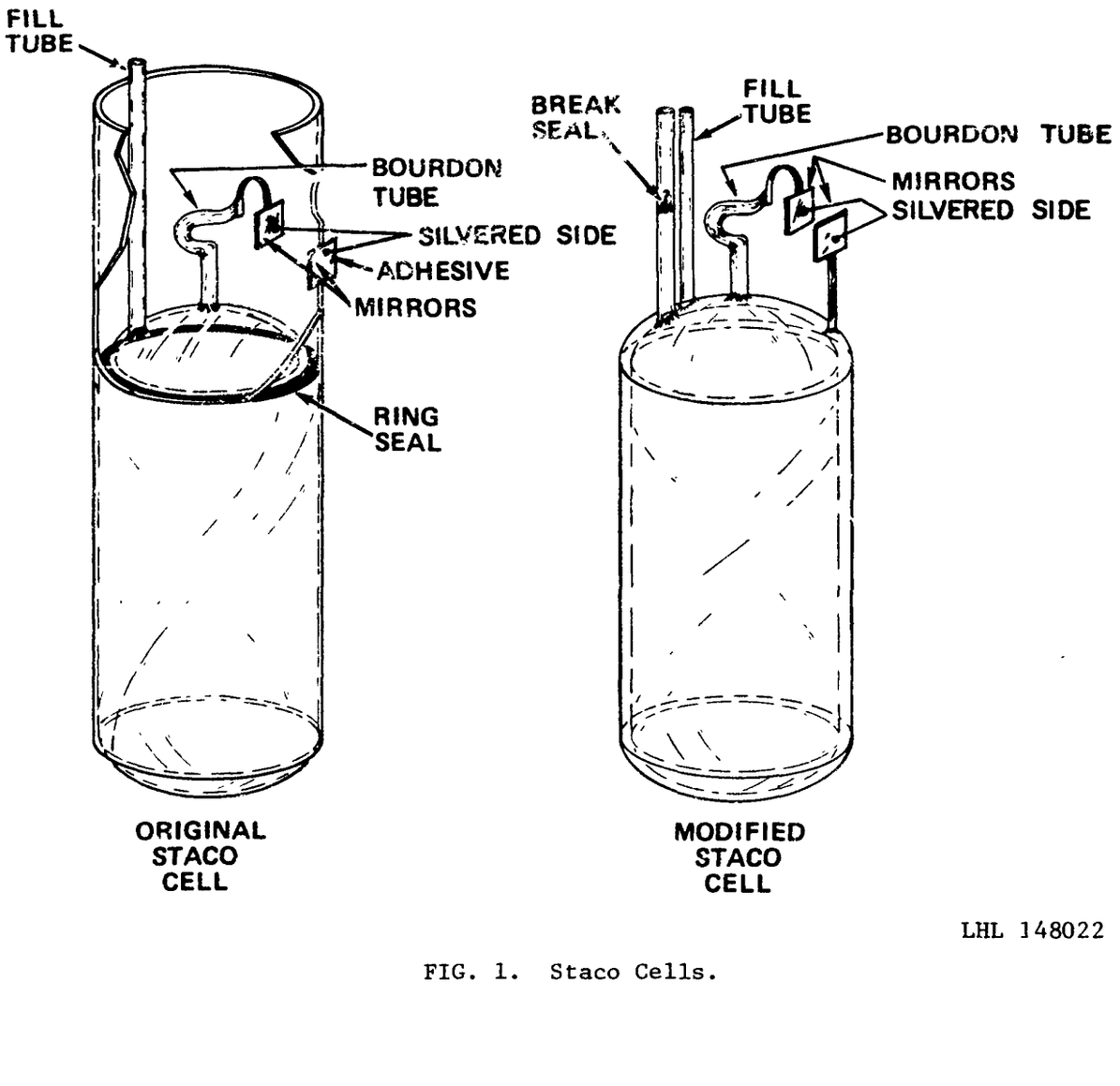

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FIG. 1. Staco Cells.

1. MILLIMETER SCALE

2. REFLECTED BEAM FROM BOURDON MIRROR (MOVES UPWARD AS PRESSURE INCREASES)

3. REFLECTED BEAM FROM GUARD TUBE (ZERO READING, DOES NOT MOVE AS PRESSURE INCREASES)

4. LASER

5. INCIDENT LASER BEAM

6. STACO CELL

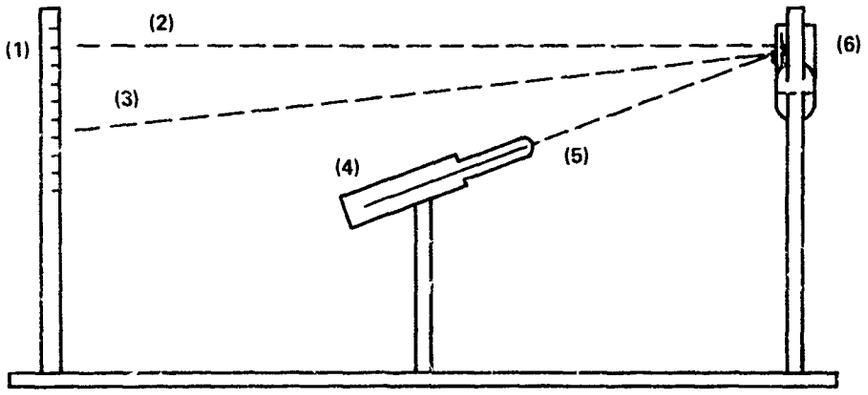

FIG. 2. Staco Cell-Laser Pressure Reading Apparatus.

4. The cells are easily handled in an inert and/or anhydrous atmosphere.

5. The glass Bourdon tube acts as a safety release since it will break at pressures slightly above the design value (40 psig).

It is felt that the Staco cells are well suited for the following studies at ambient and elevated temperatures.

1. Erosion or dissolution of samples

2. Stress corrosion

3. Surface area or dimensions of immersed samples

4. Storage-settling tests

MHF-3 liquid propellant and metal specimens are placed into Staco cells and torch sealed under an argon atmosphere. Details of loading are given under the heading; Procedures, Staco Cell Loading. They are then ready for storage in temperature controlled ovens. At intervals the cells are removed from the ovens and brought to the laboratory for

pressure measurements. The temperature of the cells was allowed to stabilize at 25°C before measurements were made. Original calibration temperature was also 25°C. For high temperature storage studies this procedure has the advantage of always using the same standard conditions at time of measurement. It has the disadvantage of temperature cycling between storage and measurement every time a reading is performed.

TEST MATERIALS

The storable liquid propellant fuel used in this study was mixed hydrazine fuel No. 3 (MHF-3), developed by the Reaction Motors Division of Thiokol Chemical Corporation (Ref. 2). Analysis of the fuel (Batch 4219) indicated that it was within specification. Analysis showed the fuel to contain 0.41 weight percent water.

The selection of metals to be evaluated in this study was based on the need for information concerning metal-propellant compatibility and also projected future needs for compatible metal containers and structural components. Table 1 lists the metals tested. These metals, supplied by Materials Research Corp., Orangeburg, N. Y., were tested in the annealed as well as the cold-worked condition because in some applications the cold-worked metal is preferred due to its increased strength. Chromium metal because of its processing history[2] and form was only tested in the annealed condition. The chromium coupons were in the form of bars, and were too brittle for further rolling. The other metal samples were rolled from bar stock on hardened steel rolls to 0.017 inches (+0.000, -0.003 inches), then all strips were annealed in vacuum - each material singly and at its own specific temperature and time (Table 2). Half of the annealed strips were further reduced 8 to 15 percent in thickness to provide specimens in the cold-worked condition. The remaining half of annealed strips were left in that condition. All pieces were cut (except for length) with metal shears before annealing to assure a minimum of cold-working. Final cutting into 10 inch strips was made at NWC, China Lake, to make the lengths compatible with the Staco cells. The nominal dimensions of the test specimens are as follows:

Annealed specimens	0.25 x 0.016 x 10 inches
Cold-worked specimens	0.25 x 0.014 x 10 inches
Chromium specimens	0.20 x 0.17 x 8.12 inches

[2]Chromium samples were produced by decomposition of high purity chromium iodide under a patent license granted to Materials Research Corporation, Orangeburg, New York, by Chromalloy American Corporation.

TABLE 1. Metals Selected for MHF-3 Compatibility Tests.

Sample no.	Metal	Metal condition
1	Titanium	Annealed
2	Titanium	Cold-worked
3	Copper	Annealed
4	Copper	Cold-worked
5	Iron	Annealed
6	Iron	Cold-worked
7	Aluminum	Annealed
8	Aluminum	Cold-worked
9	Nickel	Annealed
10	Nickel	Cold-worked
11	Chromium	Untreated
12	Chromium	Untreated

TABLE 2. Annealing Temperatures and Times.

Material	Temperature, °F	Time, hr	Cooling procedure
Titanium	1475	0.5	Furnace cooled
Copper	660	0.5	Furnace cooled
Iron	1385	0.5	Furnace cooled
Aluminum	660	0.5	Furnace cooled
Nickel	1385	0.5	Furnace cooled
Chromium[a]	...	...	...

[a]Left as fabricated

All samples were washed in acetone to remove dirt and oil. The specimens were then sealed in plastic wrap and packaged according to alloy for shipment to the Naval Weapons Center. Spectographic data furnished by the vendor show all metals to be of better than 99.99% purity. Visual examination upon receipt of the specimens in addition to microprobe analysis made at Sloan Research Industries (Ref. 3 and 4) showed the surface to be contaminated. It is doubtful that the specimens are of the purity indicated, particularly at the rolled surfaces. The sample preparation used on the received specimens prior to immersion was not sufficient to remove the foreign products. This is shown in later electron microscopic photographs.

TEST CONDITIONS

Equipment and conditions required for the pressure development phase of testing were as follows:

1. Passivated Staco cells

2. Clean specimens

3. Inert atmosphere (drybox) for handling of MHF-3 and metal specimens during filling and sealing operations, and during removal and drying of specimens at termination of pressure development tests.

4. Ullage: 25% at 25°C (77°F)

5. Storage temperature: 74°C (165°F)

6. Pressure reading temperature: 25°C

7. Test time: 94 days

8. Sample orientation: Approximately one-half of the metal specimen (5 inches) was immersed in the liquid MHF-3, leaving the other half (5 inches) exposed to the vapor.

PROCEDURES

Staco Cell Passivation

The procedure used for passivating the Staco cells was as follows:

1. Fill with 50-50 hydrazine - water.

2. Heat in water bath at 175-195°F for 1 hour.

3. Remove and let stand overnight.

4. Remove the 50-50 hydrazine - water.

5. Rinse five times with distilled water.

6. Rinse three times with electronic grade methanol (99.85% min.; Grade A Fed. Spec. O-M-232d).

7. Vacuum dry and fill with nitrogen or argon.

Propellant Handling

The MHF-3 was handled at all times under an atmosphere of dry argon.

Metal Specimen Preparation and Handling

The following procedure was followed to minimize specimen contamination upon receipt from the manufacturer:

1. Removal of one specimen of each material from its polyethylene envelope.

2. Wash in dichloromethane (methylene chloride).

3. Rinse in absolute methyl alcohol.

4. Thoroughly air dry.

5. Shear specimens to 10-inch lengths with heavy duty hand steel shears.

6. Weigh specimens.

7. Measure width, thickness, and length.

8. Seal in glass container until start of compatibility test. Each specimen was carefully cataloged and imperfections of shape and surface finish recorded. The metal specimens were transferred from the glass container to the Staco cells with plastic tongs.

Staco Cell Loading

The following steps were used in loading the Staco cells with MHF-3 and metal specimens:

1. The Staco cells were purged with dry argon and placed in drybox containing an argon atmosphere.

2. An appropriate weight of MHF-3 was added to each cell (corrected for volume of metal specimen) to fill the cell to 25% ullage.

3. The metal specimens were transferred from their pyrex holding containers to the Staco cells using plastic tongs.

4. The Staco cells were capped and removed from the drybox.

5. The Staco cells were torch sealed at the appropriate mark to correspond to 25% ullage.

6. Samples were observed for gassing, discoloration, or other abnormalities.

Pressure Readings

The Staco cells were stored at 74°C (165°F) in a heated air oven. Temperature was normally controlled to ±2.0°C. An occasional malfunction of the oven caused greater variations than this. During the first 42 days of storage, pressure readings were taken weekly. Because of mirror drift on the Staco cells due to an unsatisfactory adhesive, the weekly readings were impractical as well as inaccurate. Therefore, readings were taken after 42-, 62-, and 94-day total time periods. Pressures were determined by measuring the deflection under pressure, then breaking the cells open and allowing the Bourdon tubes to relax to their new zero pressure positions. Pressures were then determined from original deflection - pressure calibration curves. Therefore, any initial leveling off of decomposition rates with time was not evident with the first reading. In the case of chromium, however, the available data suggest that there exists an early passivation of the metal followed by an extremely low reaction rate. After measurements the cells were resealed for continuing storage at 74°C.

Metal Specimen Removal from Staco Cell

At the end of the 74°C testing period (94 days) and after taking the final pressure reading, the Staco cells containing the metal specimens were placed in an argon-filled drybox. The fill tubes were snapped off approximately 1 inch below the sealing point. The metal specimens were removed and placed in test tubes which were in turn placed in a vacuum desiccator. After drying the specimens under vacuum at 25°C for 24 hours the desiccator was filled with argon and transported to the metallographic laboratory, where testing of the specimens was initiated.

RESULTS

PRESSURE DATA

Table 3 lists the pressure development data obtained. Total storage time at 74°C (165°F) was 94 days. As previously mentioned, pressure due to propellant decomposition was measured by breaking the cell open at the filling tube and allowing the Bourdon tube to relax to its zero position, and then relating the total Bourdon deflection to previous pressure calibrations. Three such readings were taken. Figures 3 and 4 illustrate the relative rates of pressure buildup due to MHF-3 decomposition. In order of decreasing reactivity the metals compare as follows: iron, copper, nickel, chromium, aluminum, and titanium. Chromium initially reacts with MHF-3 and then apparently becomes passivated. Initial daily pressure readings, though not completely accurate because of mirror drift, indicated that this passivation occurred during the first 10 days of storage. The annealed aluminum sample also appeared to have become passivated, but only over a much longer period. In the case of the aluminum samples, only the annealed sample exhibited a pressure rise. It is suspected that a surface impurity or impurities may have been the cause. Both samples of titanium exhibited no tendency to react with MHF-3. The Bourdon tube of the Staco cell containing the annealed iron specimen fractured in storage after 62 days precluding a final pressure reading. The Staco cell containing MHF-3 only (Staco cell No. 13, Table 3) exhibited no pressure rise, indicating negligible reactivity between MHF-3 and pyrex.

In the case of each metal type, average pressure rise per day values for the two states - cold-worked and annealed was not substantially different. In most cases the annealed metal showed the greater rate. It is presently believed that variables other than heat treatment are more effective in determining the rate of fuel decomposition. Examples of such variables are metal surface contamination from the steel rolls and incomplete removal of contamination from handling.

WEIGHT CHANGES

Each specimen was weighed[3] before and after the 94-day immersion in MHF-3. All specimens underwent a small loss in weight. Values are given in Table 4. The Staco cell containing the annealed iron specimen fractured in storage and was not discovered until several hours afterwards. This resulted in severe contamination and oxidation of the specimen and MHF-3. The weight change (-0.0193 g) for this specimen should be disregarded.

[3]Weights were determined with Ainsworth balance digital type 10 N; 220 g capacity; sensitivity 0.1 mg; reproducibility ±0.03 mg.

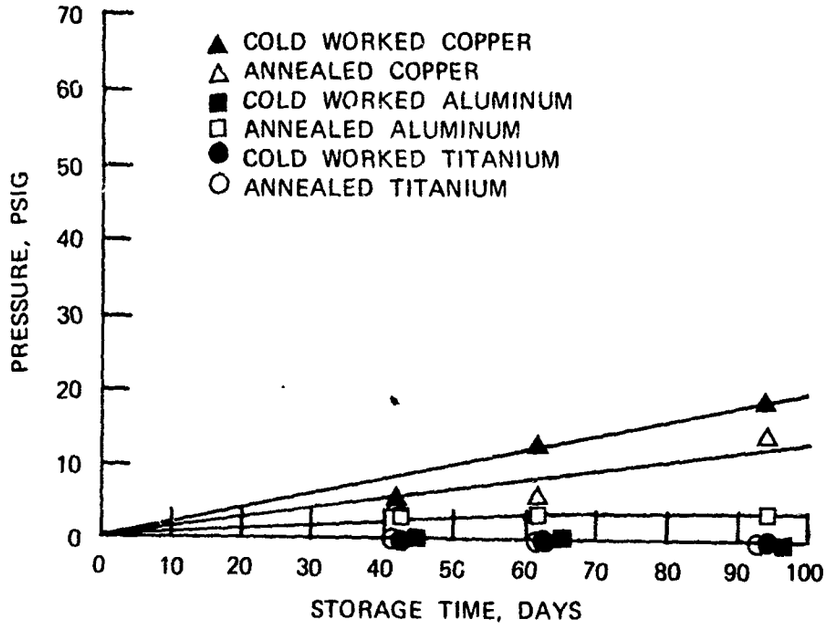

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FIG. 3. Effect of Storage Time on Pressure for Several Metal Specimens in MHF-3.

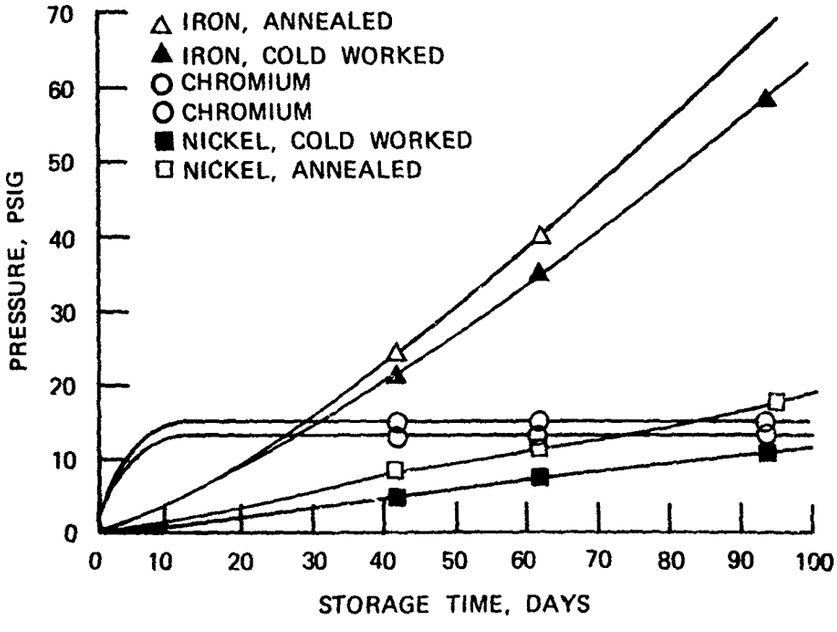

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FIG. 4. Effect of Storage Time on Pressure for Several Metal Specimens in MHF-3.

TABLE 3. Liquid Engine Materials/MHF-3 Compatibility Study.

T = 74°C (165°F), Ullage = 25% at 25°C
Total storage time = 94 days.

Staco cell no.	Sample	42 Days storage		62 Days storage (42 + 20 days)		94 Days storage (62 + 32 days)		Average psi/day for total 94 days storage (from Fig. 1-2)
		Total pressure	psi/day	Total pressure	psi/day	Total pressure	psi/day	
1	Titanium (A)	0	0	0	0	0	0	0
2	Titanium (CW)	0	0	0	0	0	0	0
3	Copper (A)	3.8	0.1	3.8	0.2	6.7	0.2	0.2
4	Copper (CW)	5.0	0.1	7.5	0.4	6.2	0.2	0.2
5	Iron (A)	23.4	0.6	16.7	0.8	...[a]	...[a]	0.6[b]
6	Iron (CW)	21.6	0.5	13.9	0.7	23.1	0.7	0.6
7	Aluminum (A)	1.8	0.4	1.8	0.1	0	0	0[c]
8	Aluminum (CW)	0	0	0	0	0	0	0
9	Nickel (A)	6.7	0.2	5.8	0.3	5.8	0.2	0.2
10	Nickel (CW)	4.5	0.1	3.1	0.2	3.9	0.1	0.1
11	Chromium	13.0	0.3	0	0	0	0	0[c]
12	Chromium	15.0	0.4	0	0	0	0	0[c]
13	MHF-3	0	0	0	0	0	0	0

NOTE: A = annealed; CW = cold-worked.

[a]Sample tube broken.

[b]62 day storage.

[c]After passivation.

TABLE 4. Weight Changes of Metal Specimens.

Metal	Condition	Weight before, g	Weight after, g	Change in weight, g
Titanium	Annealed	2.8736	2.8724	-0.0012
	Cold-worked	2.4981	2.4964	-0.0017
Copper	Annealed	6.0529	6.0523	-0.0006
	Cold-worked	5.2971	5.2959	-0.0012
Iron	Annealed	4.9323	4.9130	-0.0193
	Cold-worked	4.3744	4.3734	-0.0010
Aluminum	Annealed	1.7926	1.7916	-0.0010
	Cold-worked	1.6174	1.6174	-0.0000
Nickel	Annealed	5.6140	5.6140	-0.0000
	Cold-worked	4.8640	4.8639	-0.0001
Chromium	Annealed	34.1176	34.1160	-0.0016
	Annealed	38.6399	38.6383	-0.0016

The weight losses of the various metals do not correlate with the degree of propellant decomposition. For instance, titanium caused no pressure increase in the cell yet its weight change, compared to other metals, was relatively high. This suggests that the catalytic effect of the metal on propellant decomposition is independent of the reaction responsible for the weight change. With the exception of iron and aluminum, the cold-worked materials showed as much or greater weight losses than the annealed metals. The anomaly in the behavior of the aluminum specimens is believed to be caused from incomplete removal of contaminants from the annealed aluminum specimen prior to immersion in the MHF-3. The weight change for annealed iron is inaccurate due to premature Staco cell fracture and excessive handling.

SURFACE APPEARANCE

Visual analysis (low magnification) was made of the as-received specimens from Materials Research Corporation, Orangeburg, New York. Though all specimens were better than 99.99% pure, the surfaces showed considerable contamination. The following observations were cataloged and cited to the vendor. The vendor has offered no explanation.

Copper Specimens

A number of fingerprints showed on the surface. These marks formed a permanent record throughout testing as they could not be removed by the cleaning procedure. The fingerprints were etched into the surface of the metal from handling during metal rolling or shearing.

Iron Specimens

The iron specimens also had fingerprints from handling. Considerable amount of cold-work was present in the annealed specimen. This was verified by subsequent tensile tests. Cold-worked iron had less contamination than the annealed iron. Localized rust spots were present on all iron specimens.

Aluminum Specimens

The cold-worked specimens were not straight, making it difficult to obtain a good tensile specimen.

Titanium Specimens

Cold-worked specimens were roughened on one side giving the appearance of an "orange-peel-effect." Later pictures taken with the electron microscope indicated that abrasion of the specimen occurred during rolling.

Nickel Specimens

Cold-worked specimens showed waves normal to the rolling direction. There were many fingerprints on the cold-worked specimens. The annealed nickel specimens were much cleaner.

Chromium Specimens

Chromium specimens were of irregular cross-section (0.150 x 0.150 inches nominal dimensions), and were too irregular for tensile test coupons.

Minor differences in the surface appearance, due to MHF-3 exposure, could be observed for all of the metals tested. Visual examination indicated that the apparent change was primarily caused by differences in reflected light from the surface. However, there did appear to be a film deposit left on the specimens after testing. Because of the inability to make a quantitative evaluation, the appearance could not be correlated with material property changes.

TENSILE TESTS

Room temperature tensile tests were made for each metal and condition (annealed and cold-worked) before and after exposure. The exposed specimens were further classified into vapor and liquid exposed sections. The

tensile strength, yield strength, and percent elongation for the individual tests are given in Table 5. For ease of comparison the information has been placed in graphical form in Fig. 5.

The greatest variation in physical properties due to MHF-3 exposure may be found in the cold-worked aluminum. It may be observed that yield strength and fracture strength have decreased with a corresponding increase in elongation. The consistency in the change of properties suggests that the differences are due to the annealing of the cold-worked metal. The annealed aluminum shows an opposite trend - an increase in yield and maximum load, with a decrease in elongation. Photomicrographs of this material did not reveal any microstructural change which could account for this effect. Only two specimens of annealed aluminum were tested after exposure and two before; thus, it is possible that the differences are normal variations in testing. However, the good agreement obtained for like specimens infer real effects and strongly suggest the need for further testing, particularly for longer exposure times.

For the cold-worked titanium there is a change in properties similar to the annealed aluminum but to a lesser extent. There is an increase in the elongation of the annealed titanium but no substantial change in the other properties.

The cold-worked iron shows a drop in elongation, however strengths remain about the same. The annealed iron specimen was contaminated upon premature fracture of the Staco cell and the test values are not considered representative.

Changes in the nickel and copper specimens appear to be in the range of expected test value variation. No experimental tests were made of the chromium specimens.

MICROSTRUCTURE

Photomicrographs were taken of the as-received and exposed metals and are shown in Fig. 6 through 11. The structure of the vapor and liquid MHF-3 exposed specimens appears much the same as the as-received specimens. No indications could be found at 600 magnification that would account for a change in the physical properties. Higher magnification pictures taken with the electron microscope did reveal differences for the titanium and aluminum samples and are discussed in the following section.

ELECTRON MICROSCOPE AND MICROPROBE ANALYSIS

Both the scanning electron microscope and the electron beam microprobe (Ref. 3 and 4) were used to evaluate the extent of contamination and surface conditions of the as-received and exposed metal specimens.

TABLE 5. Tensile Tests of Compatibility Specimens.

Material	Condition	Envelope	Thickness, in	Width, in.	Area, in^2	Load yield, lb	Yield strength, psi	Maximum load, lb	Tensile strength, psi	Elongation, in.	Strain, %
Titanium	CW	a	0.0135	0.1800	.002430	77.0	31,700	87.0	35,800	.110	11.0
	CW	a	0 0132	0.1890	002495	86.0	34,500	98 0	39,300	.050	5.0
	CW	V	0 0140	0.1870	002618	115 0	43,900	123.0	47,000	.030	3.0
	CW	L	0.0135	0 1880	002538	102.0	40,200	117.0	46,100	.060	6.0
	A	a	0.0155	0.1870	.002898	21.0	7,250	62 5	21,600	220	22.0
	A	a	0.0150	0 1900	.002850	22.0	7,700	67.0	23,500	.230	23.0
	A	V	0.0150	0.190	.002850	24.5	8,600	62.0	21,800	.290	29.0
	A	L	0.0160	0 1930	.003088	28 0	9,060	67.5	21,900	.290	29.0
Copper	CW	a	0 0140	0.1895	.002653	85 0	32,000	93.0	35,000	.190	19.0
	CW	a	0.0140	0.1860	002604	86.0	33,000	92.5	35,500	.100	10.0
	CW	V	0 0140	0.1895	.002653	86.0	32,400	92.0	34,700	.090	9.0
	CW	L	0.0140	0.1870	.002618	87.0	33,400	93.5	35,700	.120	12.0
	A	a	0.0160	0.1900	003040	18.0	5,900	98.0	32,200	.310	31.0
	A	a	0.0160	0.1880	003008	17.0	5,600	97.0	32,200	.370	37.0
	A	V	0.0160	0.1900	003040	19.0	6,200	93.0	30,600	.440	44.0
	A	L	0 0170	0.1910	.003247	20.0	6,160	95.0	29,300	.300	30.0
Iron	CW	a	0 0140	0.1890	.002646	18.0	44,000	124 0	46,900	.090	9.0
	CW	a	0.0140	0.1870	.002618	110.0	42,000	117.0	44,700	.100	10.0
	CW	V	0.0140	0.1775	002485	108.0	43,500	110.0	44,300	.070	7.0
	CW	L	0 0138	0.1910	002636	118 0	44,700	122 0	46,300	.070	7.0
	A	a	0.0157	0.1890	002967	94 0	31,700	113.0	38,100	.280	28.0
	A	a	0.0152	0.1875	002850	80.0	28,100	107.0	37,500	.320	32.0
	A	V	0 0152	0.1910	002903	95 0	32,700	111.0	38,200	.360	36.0
	A	L	0.0151	0.1920	002899	86.0	29,700	107 0	36,900	350	35 0
Aluminum	CW	a	0.0145	0.1890	.002740	14 0	5,109	16 8	6,130	.090	9.0
	CW	a	0 0150	0.1850	002775	14.5	5,200	16.9	6,100	.100	10.0
	CW	V	0.0160	0.1880	003008	10 5	3,500	16.7	5,550	.270	27.0
	CW	L	0.0160	0.1875	003000	6.6	2,200	13.0	4,300	.270	27.0
	A	a	0.0100	0.1850	.003145	10.6	3,370	16.7	5,310	.240	24.0
	A	a	0.0170	0 1880	003196	9.4	2,940	16.3	5,100	.220	22.0
	A	V	0 0150	0 1880	.002820	14.0	4,960	17 0	6,030	100	10 0
	A	L	0.0150	0.1850	.002775	12 8	4,610	15 7	5,660	.110	11.0
Nickel	CW	a	0.0130	0.1860	002418	107 0	44,250	118.0	48,800	.022	2.2
	CW	a	0.0130	0.1860	002418	152.0	62,861	153.0	63,300	.016	1.6
	CW	V	0 0130	0.1900	002470	132.0	53,400	133.0	53,800	.024	2.4
	CW	L	0 0130	0 1900	.002470	145.0	58,700	147 0	59,500	.018	1.8
	A	a	0 0160	0.1890	.003024	23 0	7,600	125.0	41,300	.230	23.0
	A	a	0 0150	0 1880	002820	17 0	6,030	98 0	34,750	.220	22.0
	A	V	0 0160	0.1750	002800	35 0	12,500	104.0	37,100	.240	24.0
	A	L	0.0150	0.1890	.002835	25.0	8,820	112.0	39,500	.220	22.0
Chromium[a]	...	...	..	...	..	..	..	..	...	...	.

NOTE. CW = Cold-worked.
A = Annealed
a = Condition as received
V = Exposed to MHF-3 vapor
L = Exposed to MHF-3 liquid

[a]No chromium specimens tested.

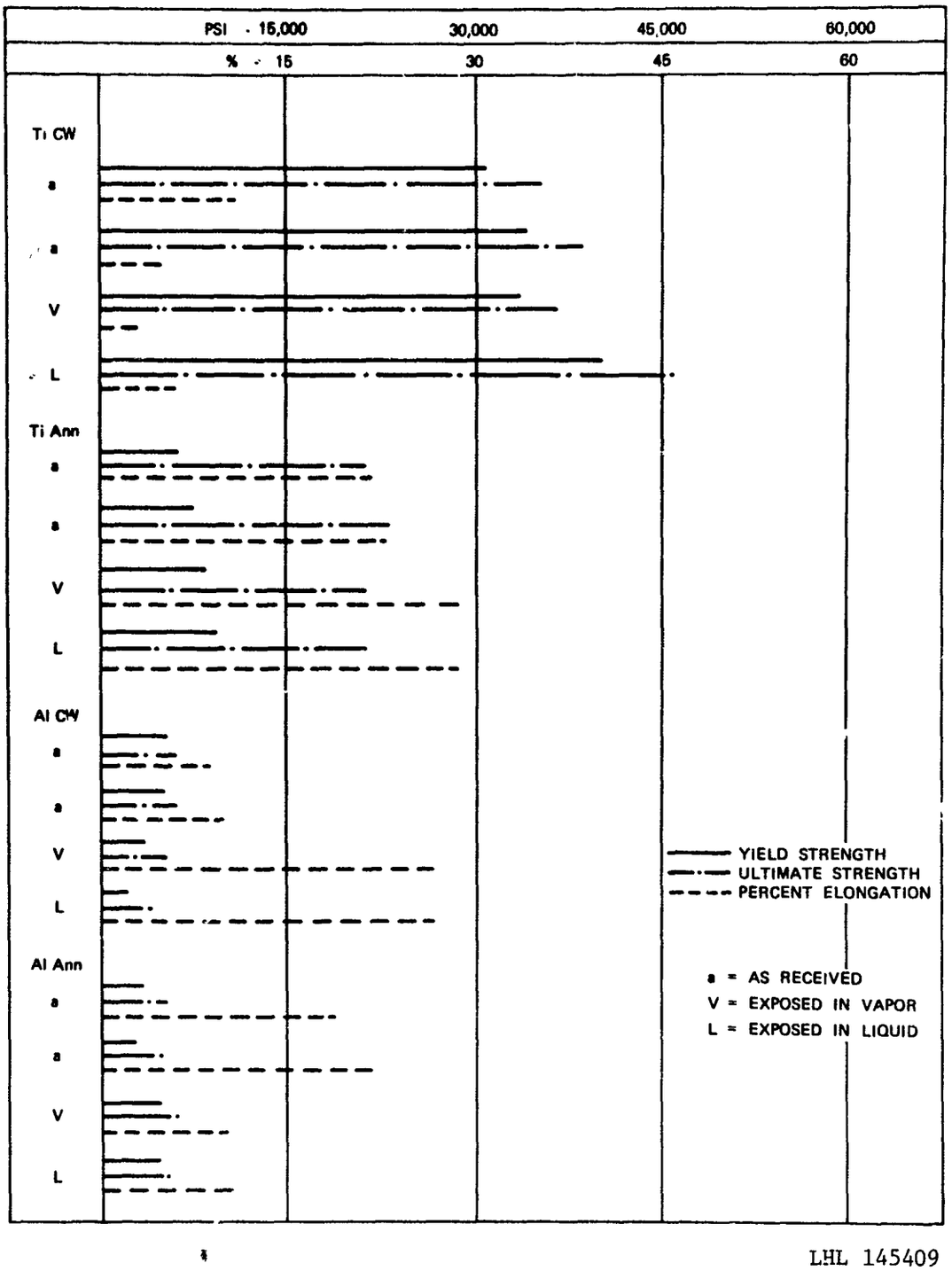
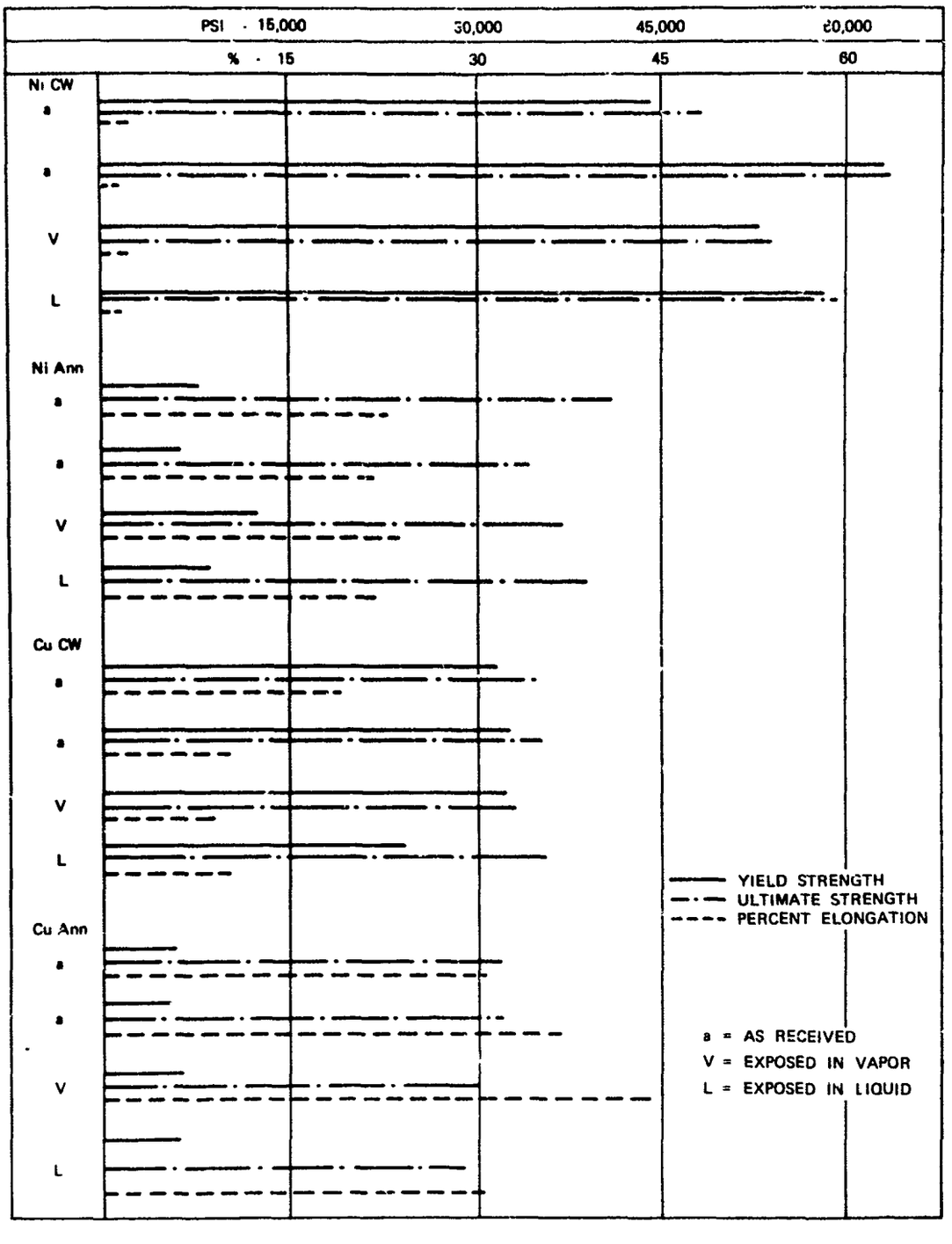
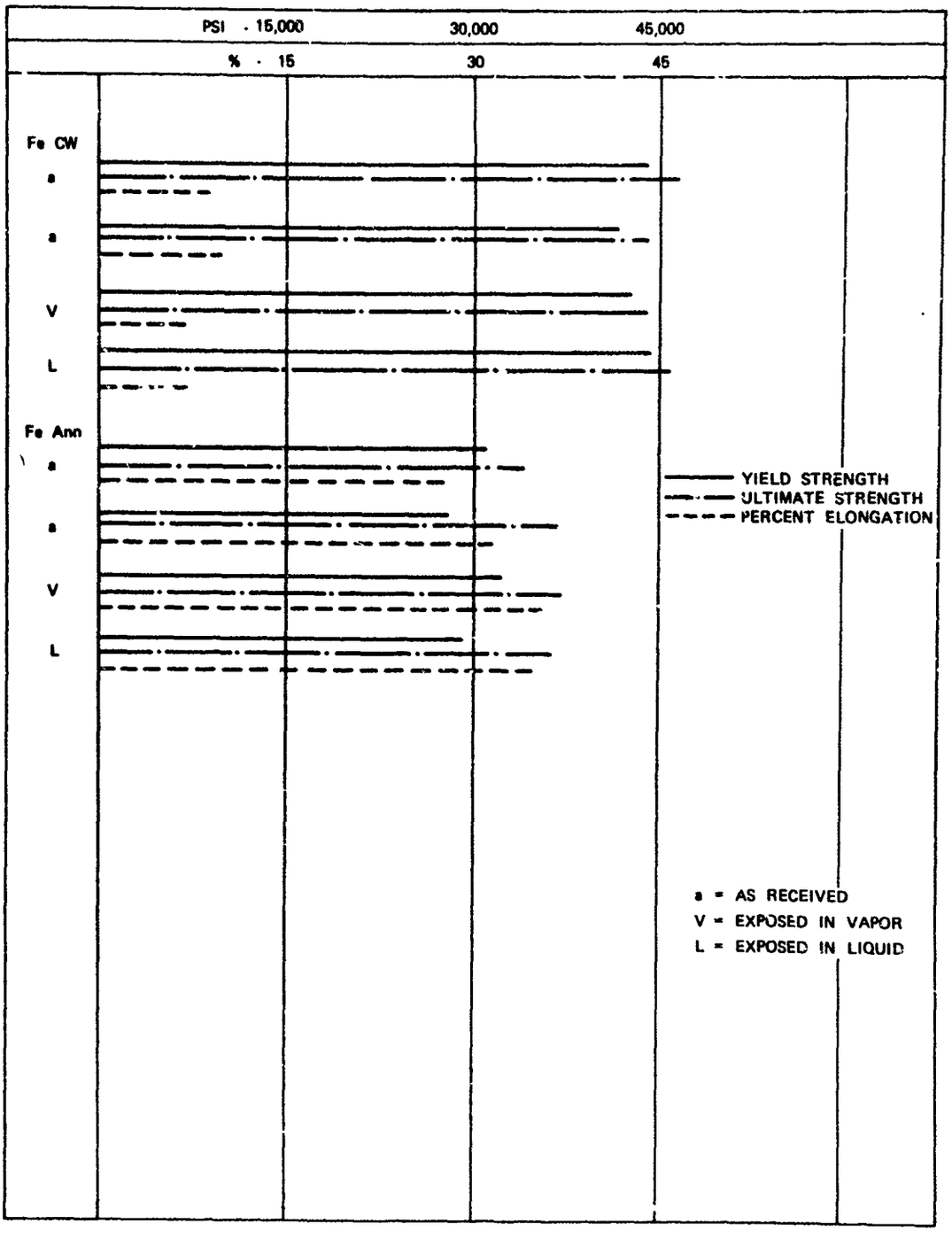


FIG. 5. Mechanical Properties of As-Received and Exposed Metal Specimens.



LHL 145410

FIG. 5. (Continued).



LHL 145411

FIG. 5. (Continued).

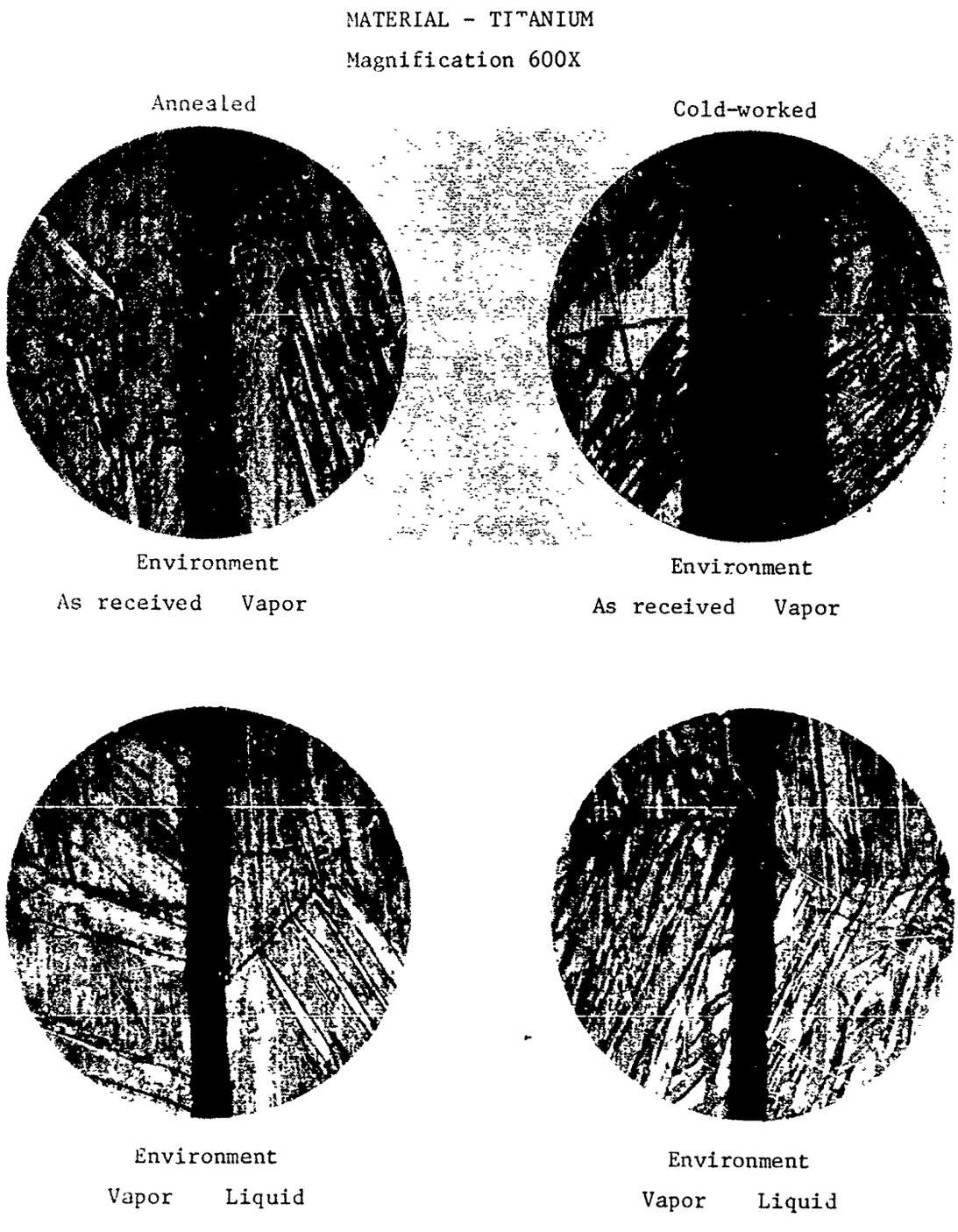


FIG. 6. Photomicrographs of As-Received and Exposed Titanium Specimens.

MATERIAL - ALUMINUM

Magnification 600X

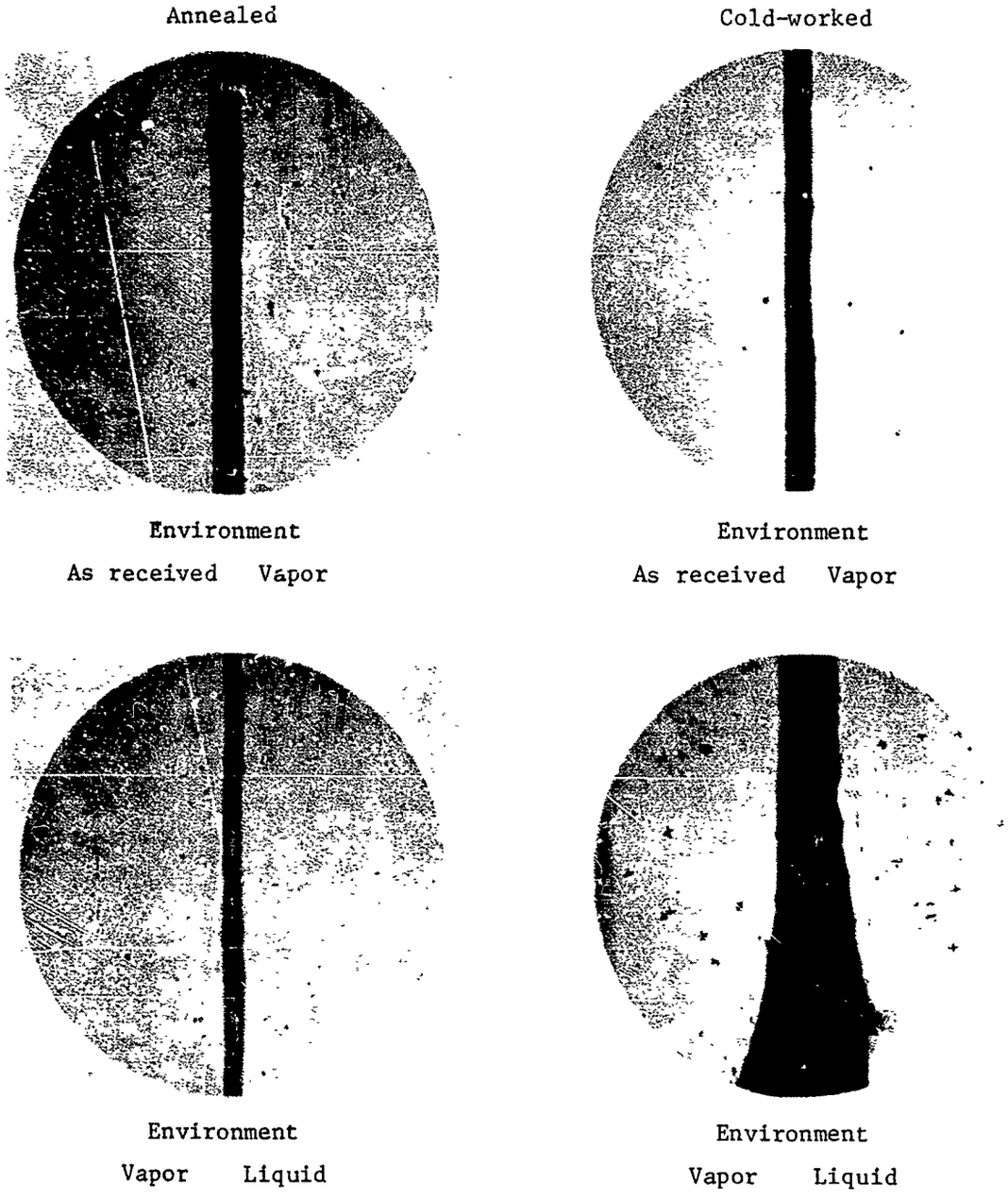
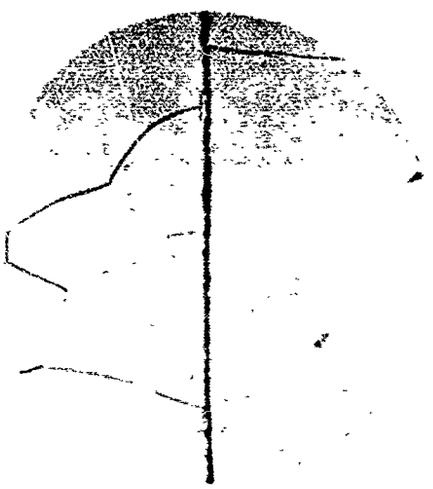


FIG. 7. Photomicrographs of As-Received and Exposed Aluminum Specimens.

MATERIAL - NICKEL

Magnification 600X

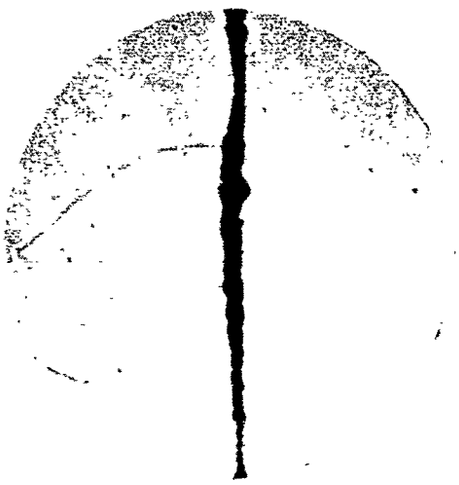
Annealed



Environment

As received Vapor

Cold-worked



Environment

As received Vapor

Environment

Vapor Liquid

Environment

Vapor Liquid

FIG. 8. Photomicrographs of As-Received and Exposed Nickel Specimens.

MATERIAL - COPPER

Magnification 600X

Annealed

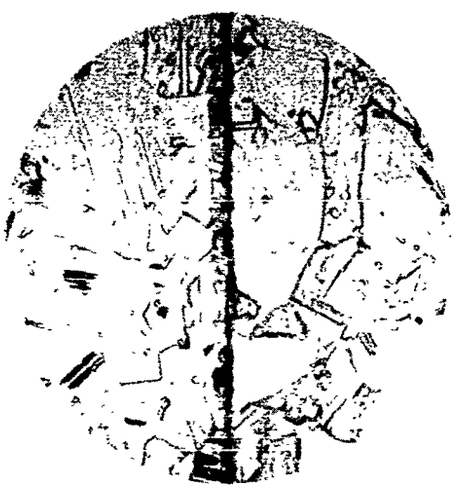
Environment

As received Vapor

Cold-worked

Environment

As received Vapor



Environment

Vapor Liquid

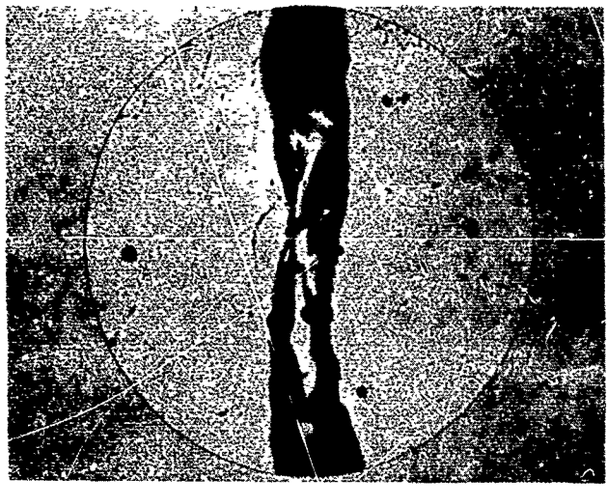
Environment

Vapor Liquid

FIG. 9. Photomicrographs of As-Received and Exposed Copper Specimens.

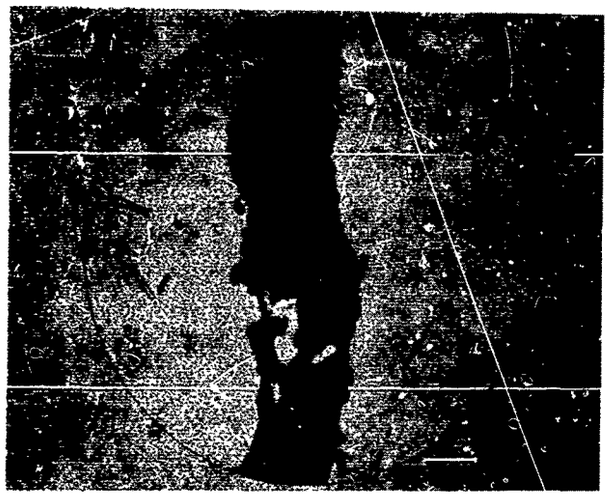
MATERIAL - CHROMIUM

Magnification 600X



Environment

As received Vapor



Environment

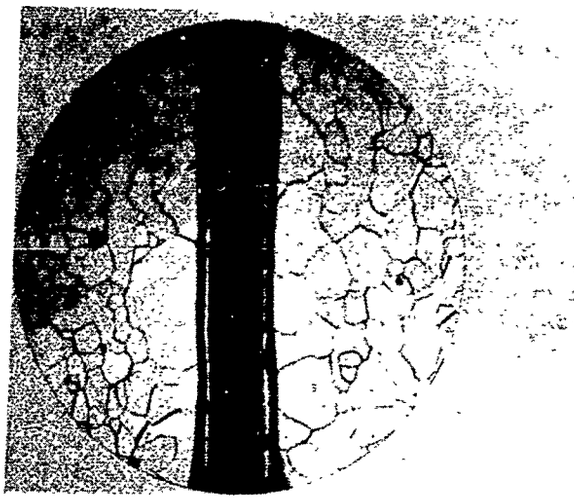
Vapor Liquid

FIG. 10. Photomicrographs of As-Received and Exposed Chromium Specimens.

MATERIAL - IRON

Magnification 600X

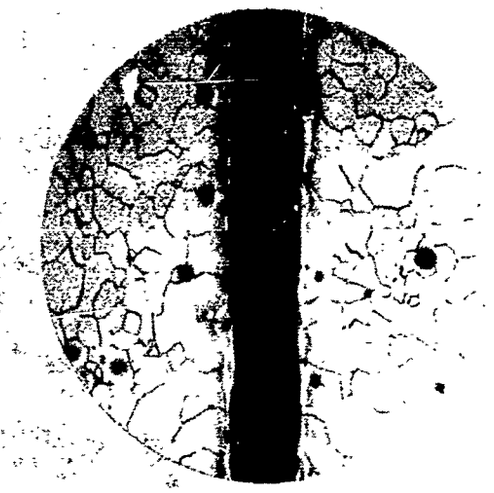
Annealed



Environment

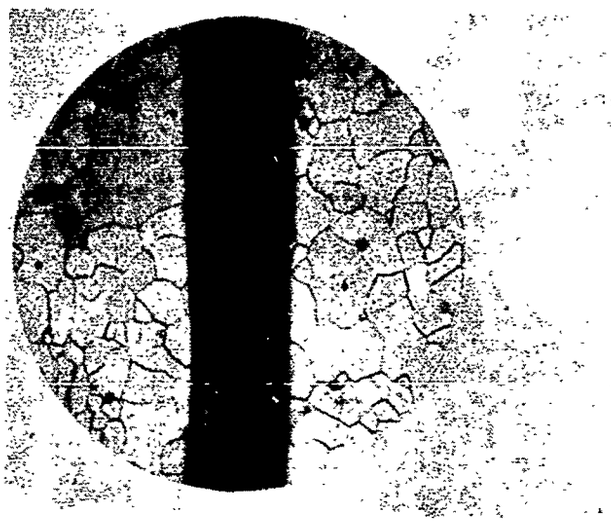
As received Vapor

Cold-worked



Environment

As received Vapor



Environment

Vapor Liquid

Environment

Vapor Liquid

FIG. 11. Photomicrographs of As-Received and Exposed Iron Specimens.

Major effort was concerned with the analysis of cold-worked and annealed titanium and aluminum because their behavior in the MHF-3 showed these to be the most likely candidates for the base metal of practical alloys for structural applications. A summary of the findings may be found in Table 6 and the pictures obtained with the scanning electron microscope are shown in Fig. 12 through 20.

The approach in making these studies was first to examine the surfaces with the scanning electron microscope to find evidence of attack or contamination and then to study these areas with the electron beam microprobe looking for concentrations of oxygen, carbon, and nitrogen.

No sample preparation was necessary other than mounting and grounding the specimen to the holder with conductive paint. After the specimens were mounted, they were examined under an optical microscope for pitted or contaminated areas. These areas were marked by scratching scribe lines in the metal surface. These areas were then examined with a scanning electron microscope using a 20 Kv beam colimated to 100 Å diameter and utilizing secondary electron mode. After representative pictures were taken of the samples, the same areas were studied with a Philips Mark I electron beam microprobe using a 15 Kv 1 micron diameter electron beam, a lead stearate analyzing crystal, a flow proportional counter using methane gas, and a pulse-height analyzer set with the proper window for each element. Figures 12 through 15 show the surfaces of the as-received titanium and aluminum taken with the scanning electron microscope; Fig. 16 through 20 show the surfaces after MHF-3 exposure.

SUMMARY

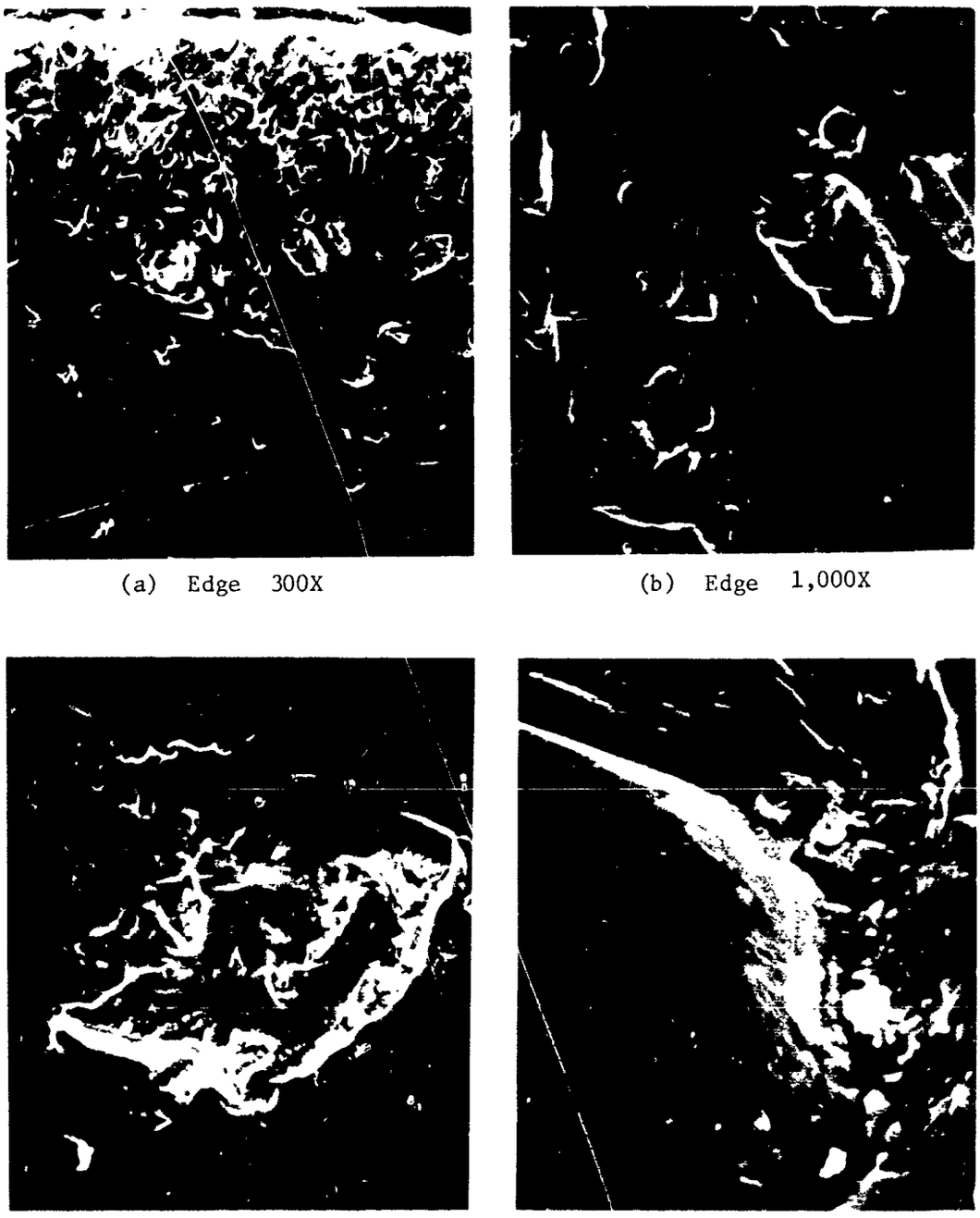
A summary of observations made by Sloan Research Industries documenting the as-received and the exposed titanium and aluminum specimens is presented in Table 6. These differences with the exception of the annealed titanium appear to be more chemical in nature rather than topographical. Annealed aluminum shows a greater amount of pitting for the exposed specimen than for the as-received (see Fig. 14 and 18). The surfaces of both annealed aluminum and titanium have some pitting in the as-received condition (Fig. 12 and 14). It is possible that such pits served as attack sites during MHF-3 exposure.

Microprobe signal variation indicates organic deposits or films present on all specimens which may be due to handling methods. Due to the large amount of contamination and surface defects present on the as-received specimens, especially the cold-worked metal, it is extremely difficult to form definite conclusions. In spite of the poor condition of the as-received specimens, no gross differences in the surface appearance between the as-received and the exposed specimens are apparent.

TABLE 6. Summary of Observations Made by Sloan Research Industries, Inc.

Titanium annealed	Titanium cold-worked	Aluminum annealed	Aluminum cold-worked
Samples as Received From Manufacturer			
Pits largely concentrated along edge - appear to be mechanically induced	Surface roughness similar to exposed specimen	Generalized pitting but not as extensive as exposed specimen	"Mud Flat" residue
At edge zone - carbon moderate to high, N_2 and O_2 were low and variable	High carbon and N_2 in both middle and edge, O_2 low in middle, low to moderate in edge zone	Edge dark spots high in carbon, low in N_2 and O_2	No "flake" type contamination
Pits in middle - carbon and O_2 moderate, N_2 low. Contamination in pits.	Some evidence of thin surface film	Pits near middle of specimen, low but uniform carbon. N_2 background level, O_2 uniform but moderate	Low concentration of O_2 on general surface
			High carbon count, low N_2, moderate O_2 in contaminated regions (Fig. 15)
Samples Exposed to MHF-3 Liquid or Vapor			
Pits (Fig. 16a and b)	General surface roughness (Fig. 17d)	Corrosion pits in both liquid and vapor regions	"Mud Flat" residue (Fig. 19b and c)
"Blob type" deposits sometimes accompany pits (Fig. 16c)	Moderate to high O_2 and N_2, very high carbon in rough areas	Residue in pits shows high carbon, moderate O_2, minor N_2	Pits (Fig. 20a)
No carbon or N_2 was found in pits or blobs. O_2 level similar to background level	Overall surface shows O_2 background	General area away from pits shows some O_2 present	Flake type contamination in material exposed to vapor (Fig. 20a)
Small protrusions; contains high carbon, O_2, and minor N_2 sparsely scattered on general surface (Fig. 16d)		No general residue	High background signal of O_2 on general surface; high concentration of O_2; carbon and N_2 in "Mud Flat" region

ANNEALED TITANIUM



(a) Edge 300X

(b) Edge 1,000X

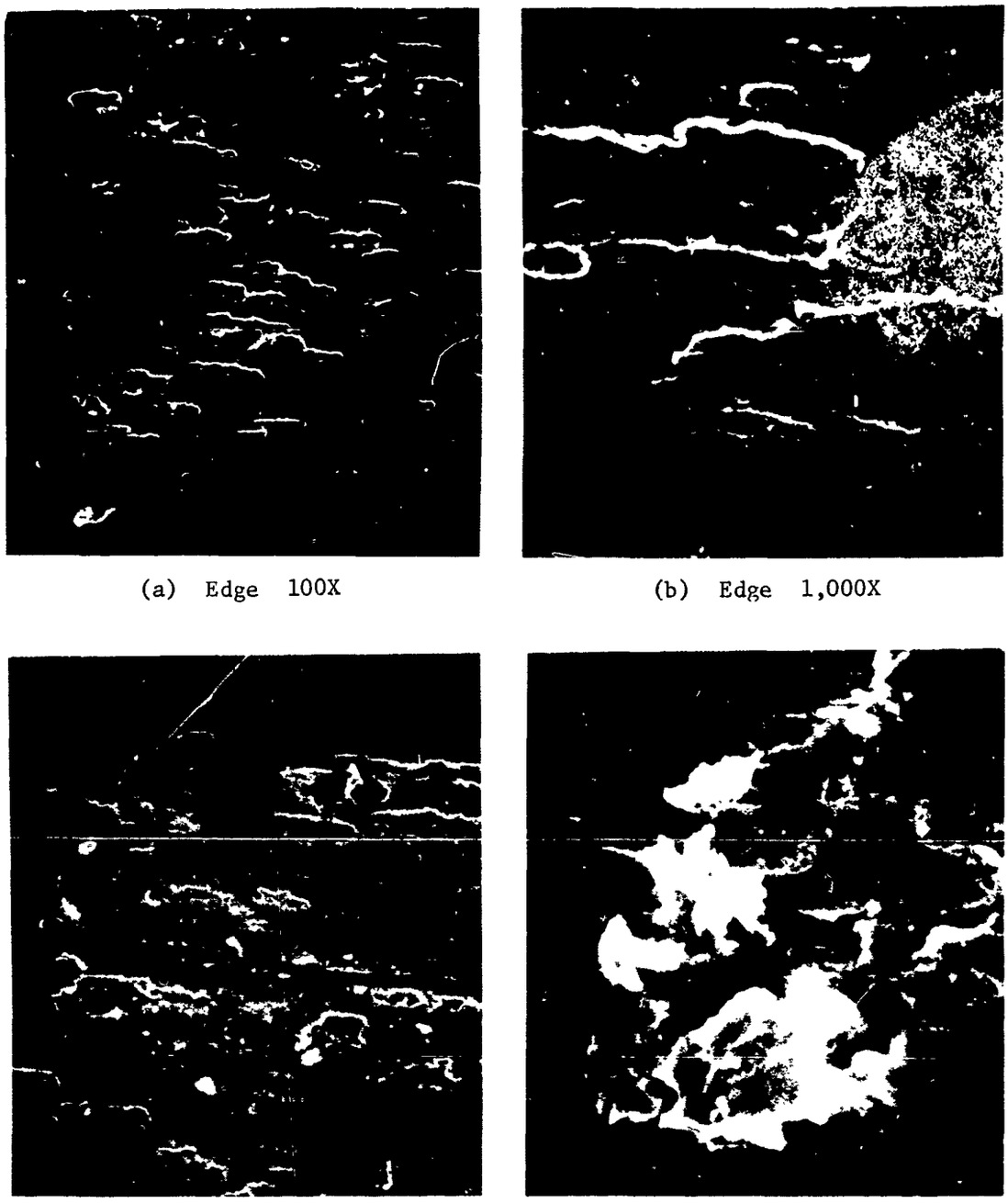
(c) Middle 1,000X

(d) Middle 4,000X

LHL 146757

FIG. 12. As-Received Annealed Titanium Specimen.

COLD-WORKED TITANIUM



(a) Edge 100X

(b) Edge 1,000X

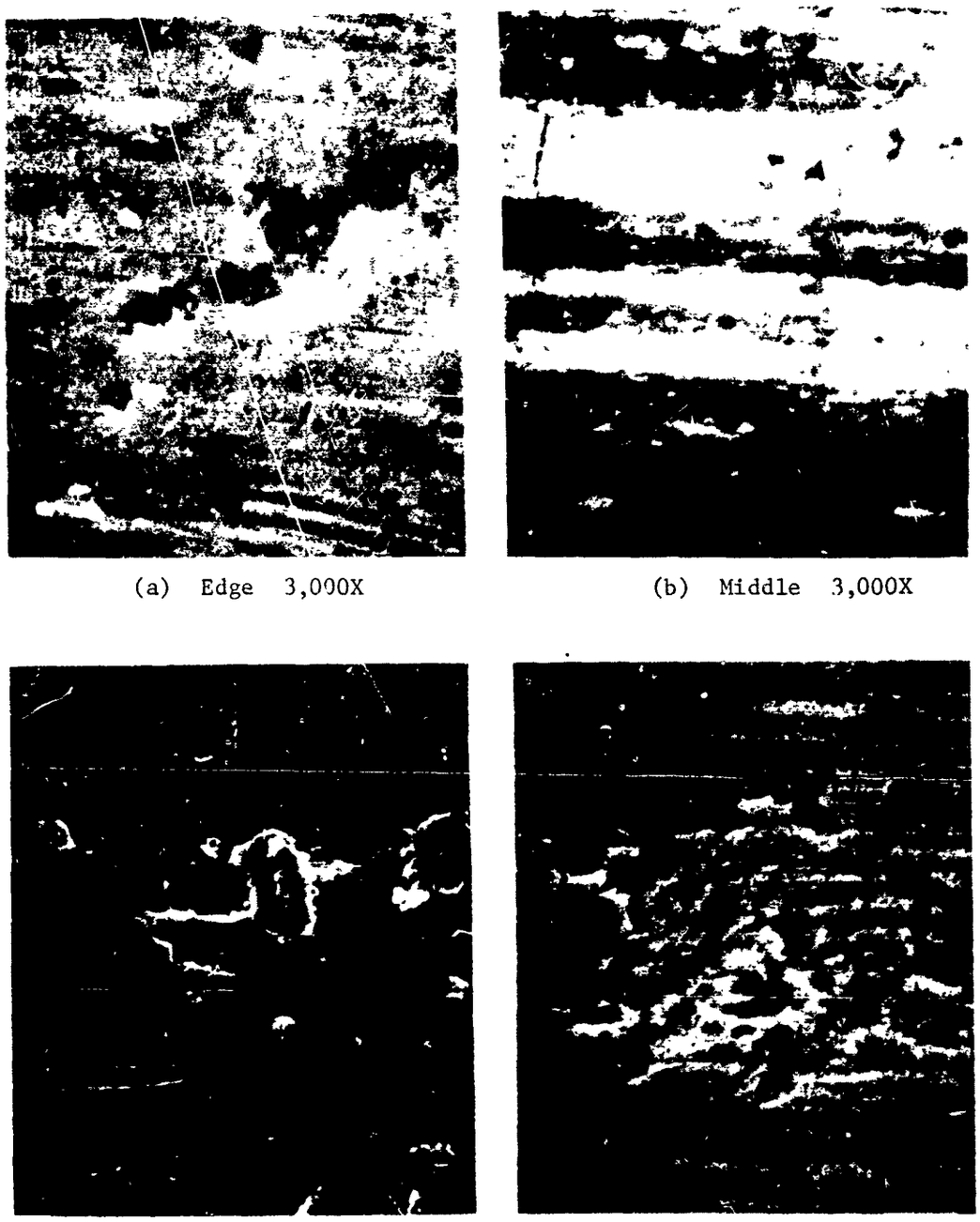
(c) Middle 100X

(d) Middle 2,000X

LHI. 146755

FIG. 13. As-Received Cold-Worked Titanium Specimen.

ANNEALED ALUMINUM



(a) Edge 3,000X

(b) Middle 3,000X

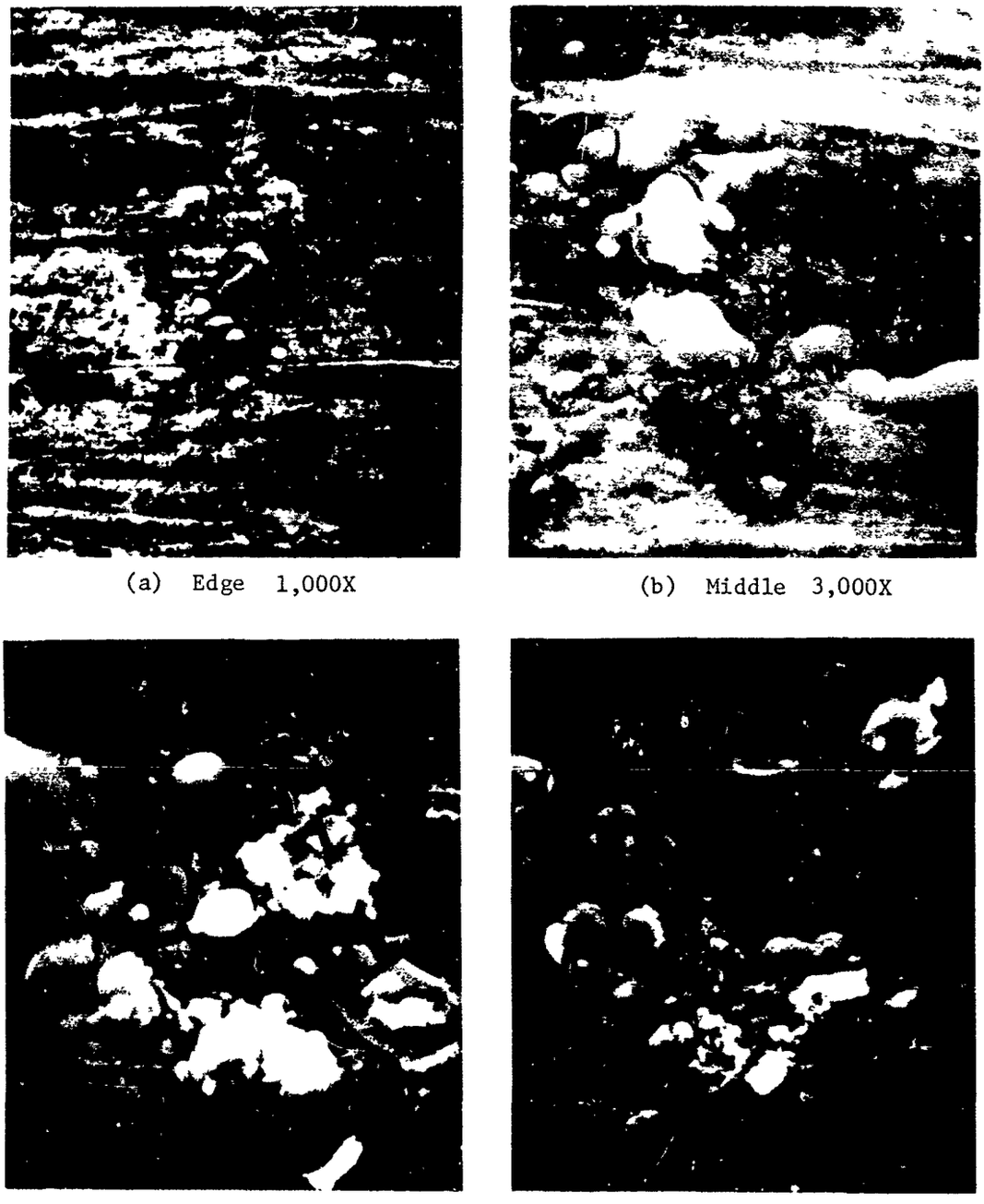
(c) Middle 3,000X

(d) Middle 1,000X

LHL 146756

FIG. 14. As-Received Annealed Aluminum Specimen.

COLD-WORKED ALUMINUM



(a) Edge 1,000X

(b) Middle 3,000X

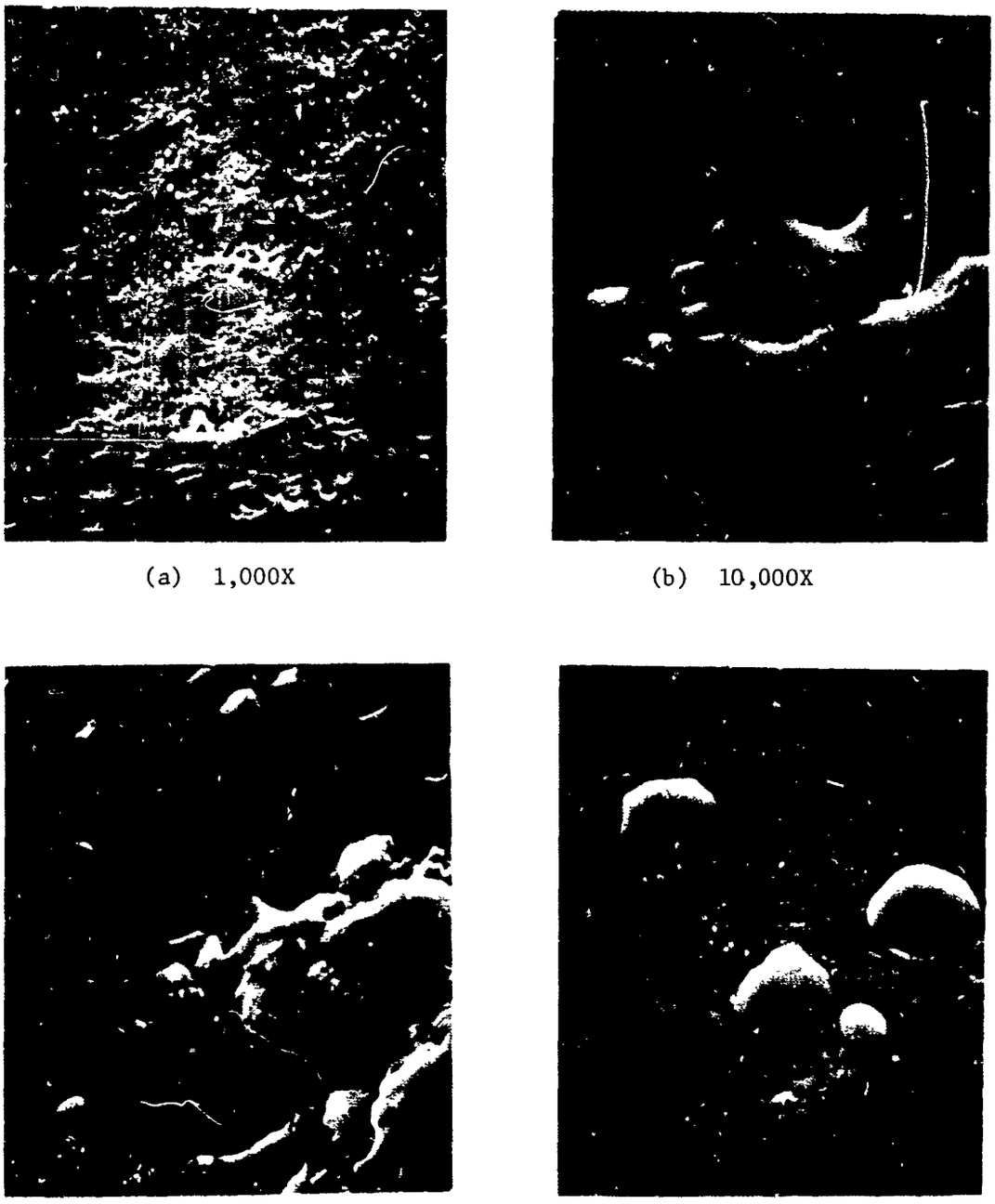
(c) Middle 3,000X

(d) Middle 3,000X

LHL 146754

FIG. 15. As-Received Cold-Worked Aluminum Specimen.

SAMPLE #1, ANNEALED TITANIUM



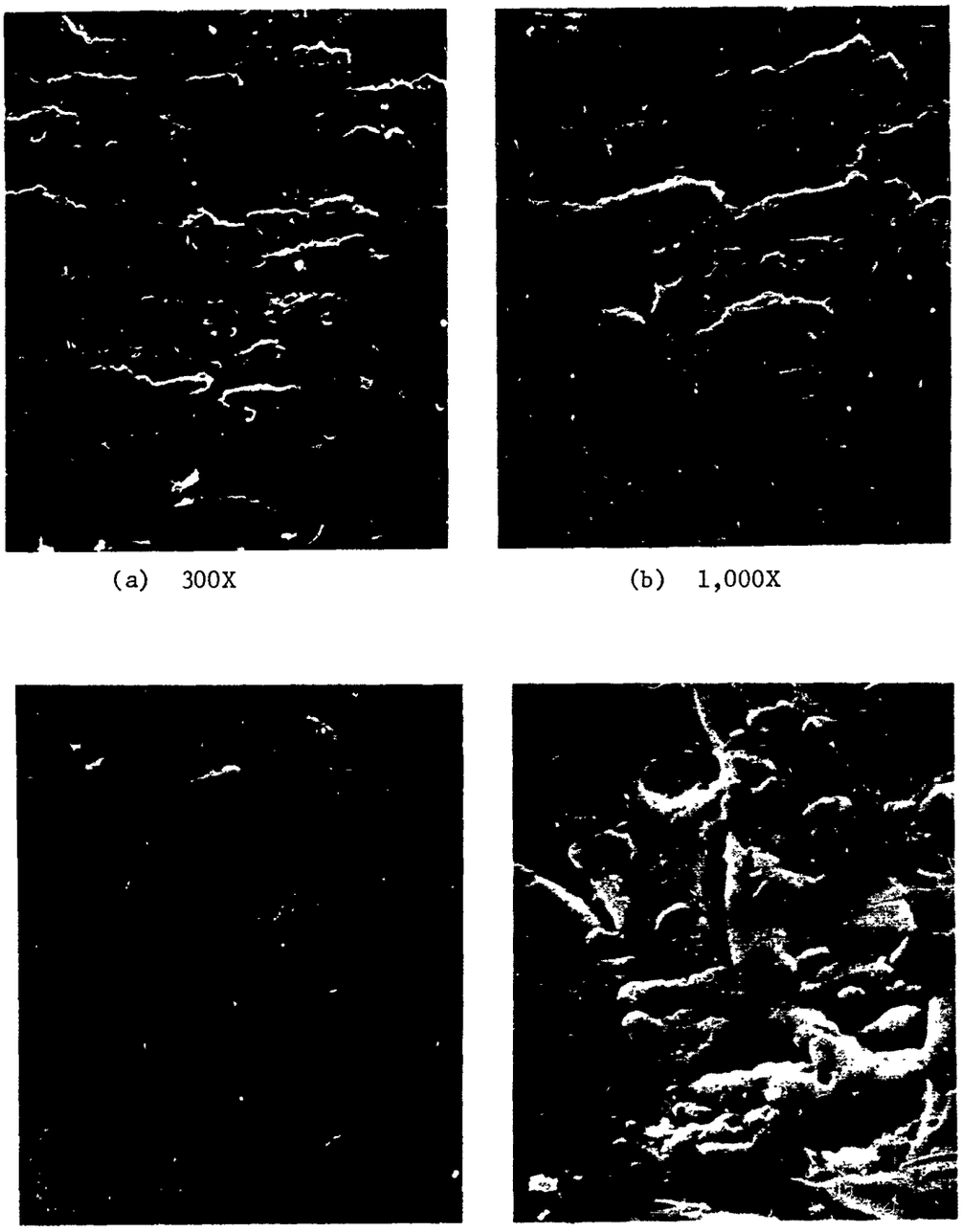
(a) 1,000X (b) 10,000X

(c) 10,000X (d) 2,000X

LHL 145382

FIG. 16. Exposed Annealed Titanium Specimen.

SAMPLE #2, COLD-WORKED TITANIUM



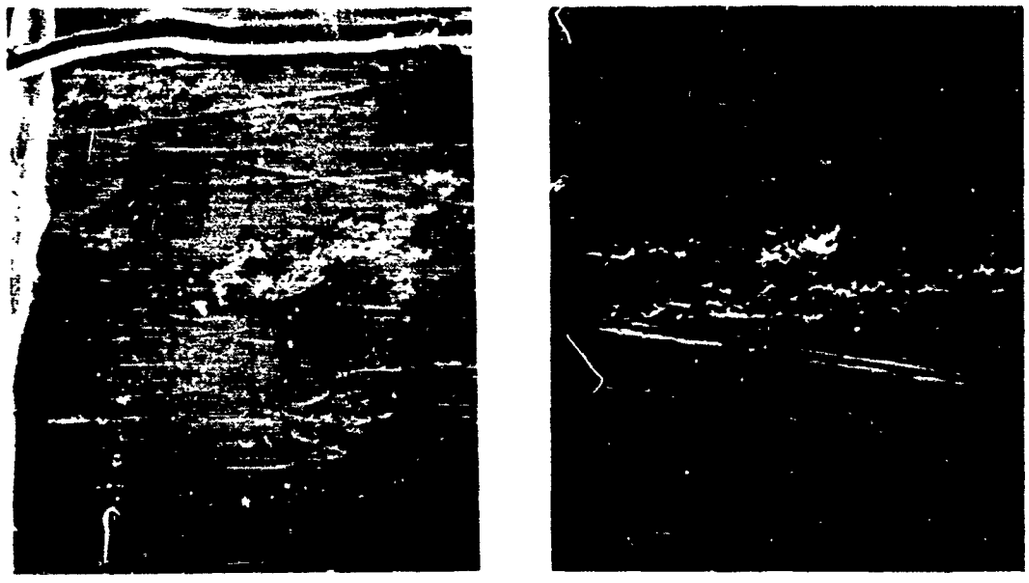
(a) 300X (b) 1,000X

(c) 2,000X (d) 3,000X

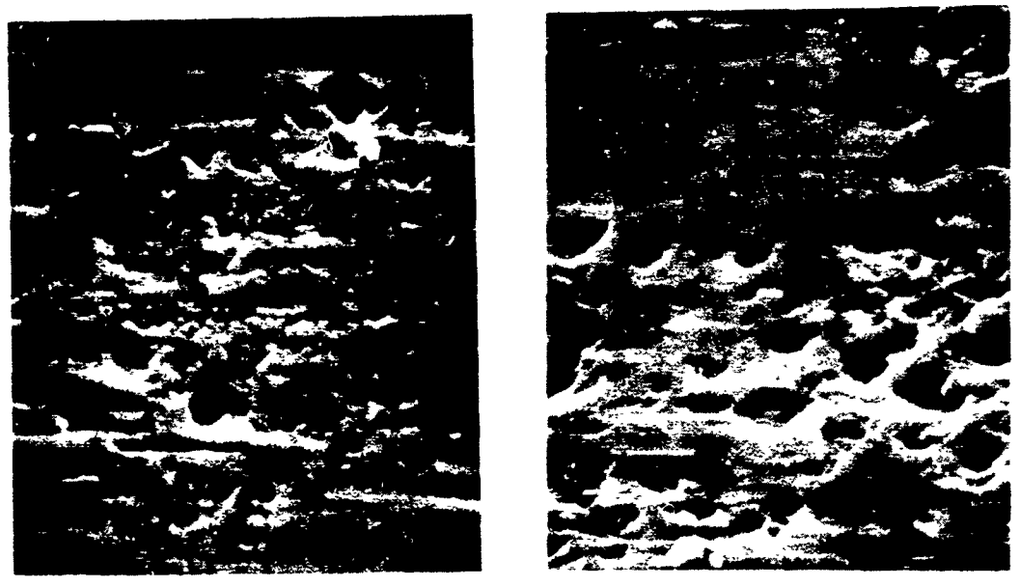
LHL 145383

FIG. 17. Exposed Cold-Worked Titanium Specimen.

SAMPLE #7, ANNEALED ALUMINUM



(a) 200X (b) 500X



(c) 2,000X (d) 3,000X

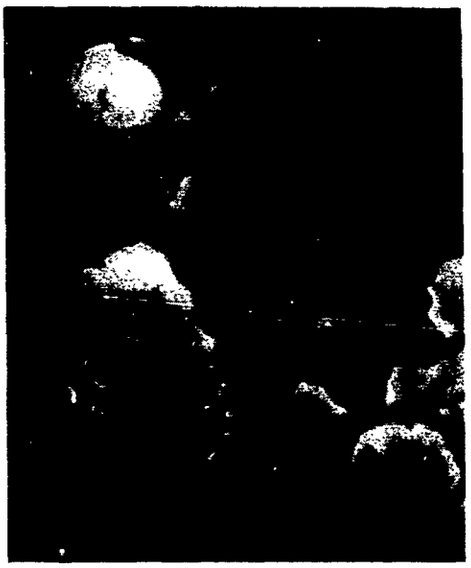
LHL 145381

FIG. 18. Exposed Annealed Aluminum Specimen.

SAMPLE #8, COLD-WORKED ALUMINUM

(a) 300X

(b) 1,000X



(c) 3,000X

LHL 145384

FIG. 19. Exposed Cold-Worked Aluminum Specimen.

SAMPLE #8, COLD-WORKED ALUMINUM

1,000X

1,000X

LHL 145957

FIG. 20. Exposed Cold-Worked Aluminum Specimen.

CONCLUSIONS

Pressure measurements were conducted during exposure of several 99.99% pure metals to MHF-3 liquid and vapor. Reactivity, as shown by the decomposition rate of the fuel, decreased in the following order: iron, copper, nickel, chromium, aluminum, and titanium.

Tensile tests conducted on the as-received and exposed metals showed that strength and ductility changed in aluminum and, to a lesser extent, with titanium after MHF-3 exposure. All other metals tested showed no property changes greater than the expected variation of testing. It is believed that the high temperature exposure (74°C) is more responsible for the change (due to annealing) in the cold-worked metal than contact with MHF-3. Strengthening of the exposed annealed aluminum and cold-worked titanium cannot be explained without further testing. In light of these results, it would be well-advised to explore the observed effects on titanium and aluminum more extensively. No correlation is evident between changes in physical properties and rate of fuel decomposition.

RECOMMENDATIONS

Due to the interest in aluminum and titanium metal as storage containers for liquid propellants and components for liquid engines, these metals should be re-tested for longer exposure times. Alloys of aluminum and titanium, representative of commercial structural materials, should also be included to determine if the more complicated structures follow the trend shown by the base metals.

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3. Sloan Research Industries, Inc. *The Scanning Electron Microscopic and Electron Beam Microprobe Studies of Two Titanium and Two Aluminum Samples*. Santa Barbara, Calif., 12 November 1969. (Report No. 963111.)

4. ------. *The Scanning Electron Microscopic and Electron Beam Microprobe Studies of Two Titanium and Two Aluminum Samples*. Santa Barbara, Calif., 19 January 1970. (Report No. 078110.)

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13 ABSTRACT

The compatibility of various pure metals with MHF-3 was determined at 74°C (165°F). Metals investigated included titanium, copper, iron, aluminum, and nickel in the annealed and cold-worked conditions, and chemically deposited chromium. Tests were conducted in an all pyrex, torch-sealed pressure vessel. Pressure changes were recorded over a 94 day period. Post exposure evaluations of the metals were made by electron microscopic examination, microprobe analysis, and tensile tests.

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	ROLE	WT	ROLE	WT	ROLE	WT
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Fuel Decomposition						
Material Testing						